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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN  
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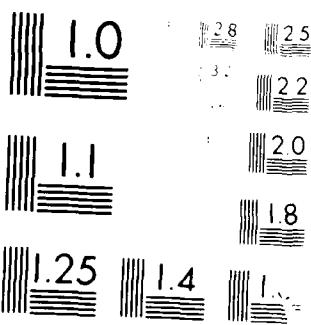
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ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS  
IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

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DAJA45-85-C-0026

Final Report, 1st year  
July 1985 - June 1986

FEB 1 7 1988

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## ENHANCED OXIDATION AND SOLVOLYSIS REACTIONS IN CHEMICALLY INERT MICROHETEROGENEOUS SYSTEMS

### SUMMARY

The quantitative analysis of in microemulsions dissolved hydrogen peroxide has been worked out for concentrations ranging from 8 M to  $10^{-7}$  M.

The stability of microemulsions containing sodium laurate, sodium dodecyl sulfate and benzyl-dimethyl-tetradecylammonium chloride as surfactants, n-butanol and t-butanol as cosurfactants as well as cyclohexane and water towards hydrogen peroxide has been investigated by kinetic measurements. These investigations involve the volumetric analysis of the oxygen evolution and the determination of the total consumption of hydrogen peroxide. Mechanistic interpretations fit with our working hypothesis calling for an efficient trapping of hydroxyl radicals by the cosurfactants.

The results imply that microemulsions containing SDS are of maximum stability (equivalent to that of aqueous solutions of hydrogen peroxide) and might be used as a reaction medium for non-catalyzed oxidation reactions not involving hydroxyl radicals. Microemulsions containing sodium laurate as a surfactant enhance hydrogen peroxide decomposition by more than a factor of  $10^3$ , and research using corresponding perfluorinated components will continue.

Our method of analysis might also be of potential use for the differentiation of oxidation reactions of hydroxyl radicals and superoxide, respectively.

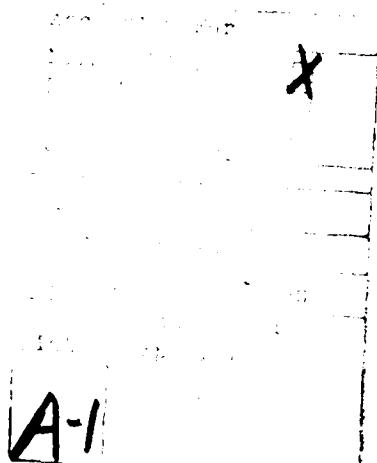
The kinetics of the oxidation of N-methyl phenothiazine (organic sulfide) with singlet oxygen has been investigated in a O/W and a W/O microemulsion and compared to the results in solution. These investigations allow to evaluate limits of the enhancement of singlet oxygen reactions with sulfides due to the microheterogeneous environment. In fact, these limits are imposed by the competing processes of chemical reaction and physical deactivation.

## SHORT TERM PROJECTS

Perfluorinated microemulsions containing carboxylates as surfactants will be worked out and tested for the enhancement of hydrogen peroxide decomposition and, consequently, for their use as reaction medium.

Kinetic investigations of the oxidation of hydrocarbons by hydroxyl radicals will be carried out, and enhancement effects attributed to solubilization or aggregation (high local concentration due to the microheterogeneous character of the reaction medium).

Stability tests with perborate will be undertaken and the results compared to those of the already reported experiments with peroxide.

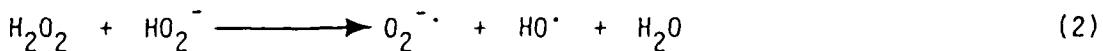
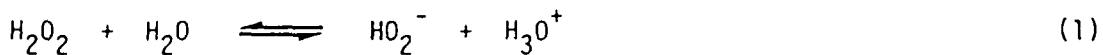


## 1. Quantitative analysis of hydrogen peroxide ( $> 10^{-4}$ M) in microemulsions

High concentrations of hydrogen peroxide ( $> 10^{-4}$  M) can be titrated with aqueous potassium permanganate ( $10^{-1}$  N); titrations are carried out as already described in the second periodic report<sup>1</sup>. Due to the acquired experience and the standardization of method and equipment used, the limit of error has been reduced to  $\pm 1,5\%$ .

## 2. Hydrogen peroxide decomposition in different O/W microemulsions

Thermal decomposition of hydrogen peroxide at temperatures used in this study is initiated by the dismutation reaction between its protonated and the deprotonated form (reactions 1 and 2).

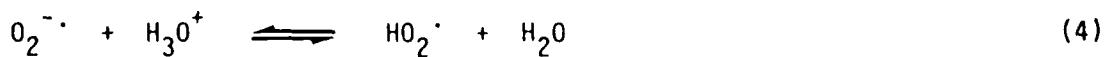


In the chosen environment, hydroxyl radicals will react with the organic material present in relatively high concentrations (surfactant, cosurfactant, hydrocarbon) and, hence, are chemically trapped (reaction 3).



The consecutive reactions of  $\text{R}^\cdot$  and their impact on our working hypothesis will be discussed below.

The superoxide anion formed in reaction 2 is in equilibrium with its protonated form (reaction 4),



an intermediate which dismutates with high rate<sup>2</sup> according to reaction 5.



If the hydroxyl radical is efficiently trapped and further reactions of the alkyl radicals formed would be of no consequence to this scheme of reactions, the final balance indicates that for one molecule of  $\text{O}_2$  formed three molecules of  $\text{H}_2\text{O}_2$  are decomposed. The same ratio must then be found between the rates of oxygen evolution and hydrogen peroxide decomposition, respectively.

Figure 1 shows the kinetic results of  $\text{H}_2\text{O}_2$  decomposition in different media. The data show clearly that the decomposition of  $\text{H}_2\text{O}_2$  in microemulsions containing either SDS or benzyl trimethyl tetradecylammonium chloride as a surfactant is negligible within the period of observation (< 240 h, 15°); the same result has also been observed under similar experimental conditions for the decomposition of an aqueous standard solution of  $\text{H}_2\text{O}_2$  (30%). In contrast, the decomposition of  $\text{H}_2\text{O}_2$  is catalyzed in microheterogeneous systems containing sodium laurate, the corresponding rates being shown in table 1.

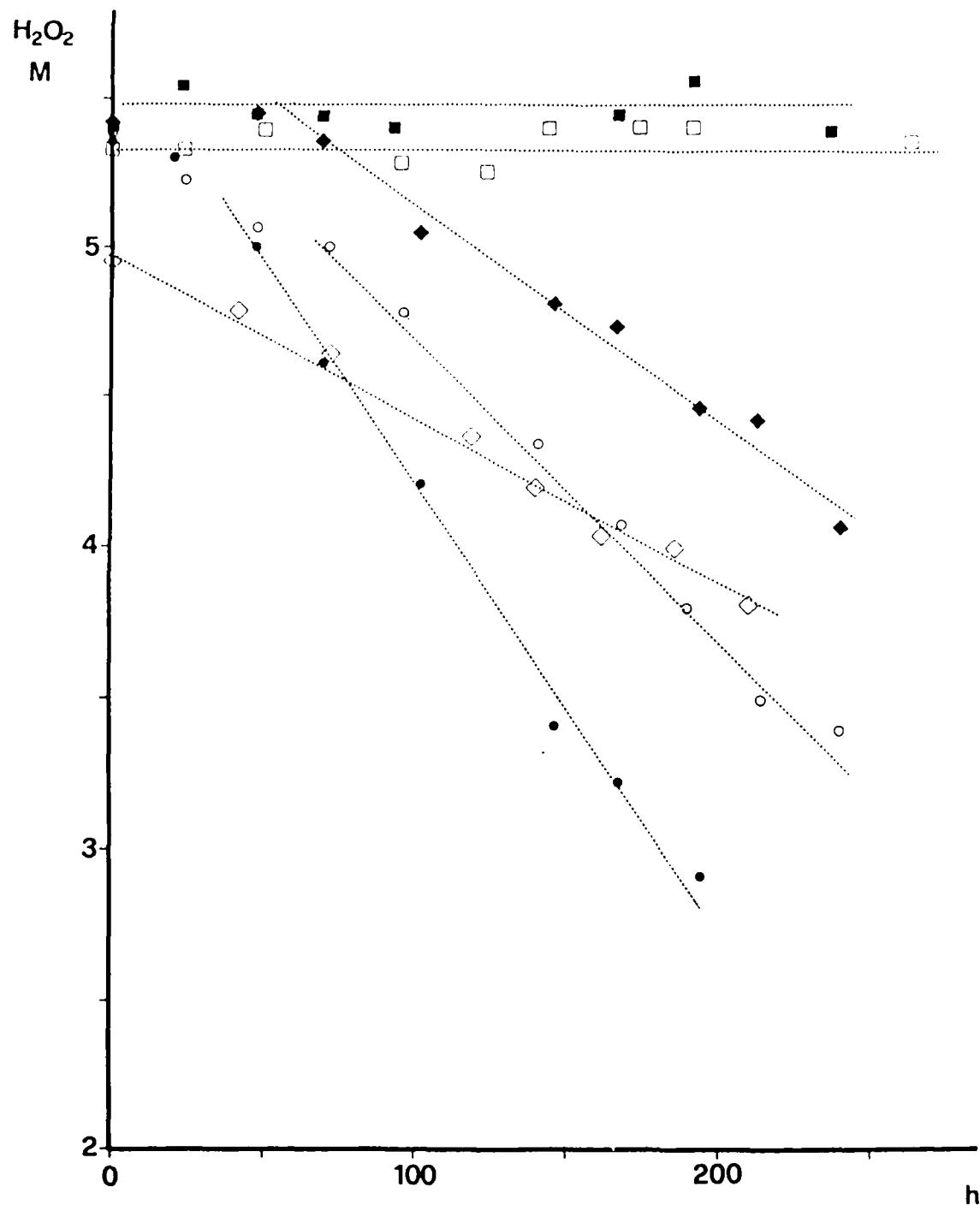
Table 1. - Rates of decomposition of  $\text{H}_2\text{O}_2$  in different microemulsions<sup>f</sup> at 15°C

A	$(4.15 \pm 0.25) \times 10^{-6} \text{ M s}^{-1}$
B	$(2.85 \pm 0.31) \times 10^{-6} \text{ M s}^{-1}$
C	$(1.52 \pm 0.11) \times 10^{-6} \text{ M s}^{-1}$
D	$10^{-8} \text{ M s}^{-1}$
E	$10^{-8} \text{ M s}^{-1}$

<sup>f</sup> s. figure 1

The enhancement of the decomposition of  $\text{H}_2\text{O}_2$  can be attributed to the characteristics of the ionic surfactant aggregate; if this aggregate is swollen by an approx. sixfold concentration of cosurfactant (B), the rate of the decomposition of  $\text{H}_2\text{O}_2$  is reduced by a factor of 1.5 (table 1).

Figure 1. - Decomposition of  $H_2O_2$  in different O/W microemulsions: A<sup>2</sup> (●), B<sup>a</sup> (○), C<sup>b</sup> (◇), D<sup>c</sup> (◆), E<sup>d</sup> (■), F<sup>e</sup> (□); 15°C



<sup>a</sup> like A, but sodium laurate/n-butanol 1 : 2

<sup>b</sup> like B, but n-butanol substituted by t-butanol

<sup>c</sup> like B, experiments made in an open vessel (s. text)

<sup>d</sup> like B, but sodium laurate substituted by sodium lauryl sulfate (SDS)

Enhancement is even more reduced when t-butanol is used as a cosurfactant instead of n-butanol.

Furthermore, it is interesting to note that the decomposition of hydrogen peroxide in microemulsions containing n-butanol shows a period of initiation of about 30 h (at 15°C), whereas in microemulsions containing t-butanol, this initiation of the  $H_2O_2$  decomposition is practically not detectable.

The mechanistic scheme explained above is indicating the importance of simultaneous measurements of  $H_2O_2$  decomposition and  $O_2$  evolution as a means for a better understanding of this complex redox system. Figure 2 shows the results of the corresponding volumetric oxygen measurements. Again, oxygen production in microemulsions D and E is negligible, hence, confirming the stability of hydrogen peroxide in those media. The calculated rates of oxygen evolution are shown in table 2.

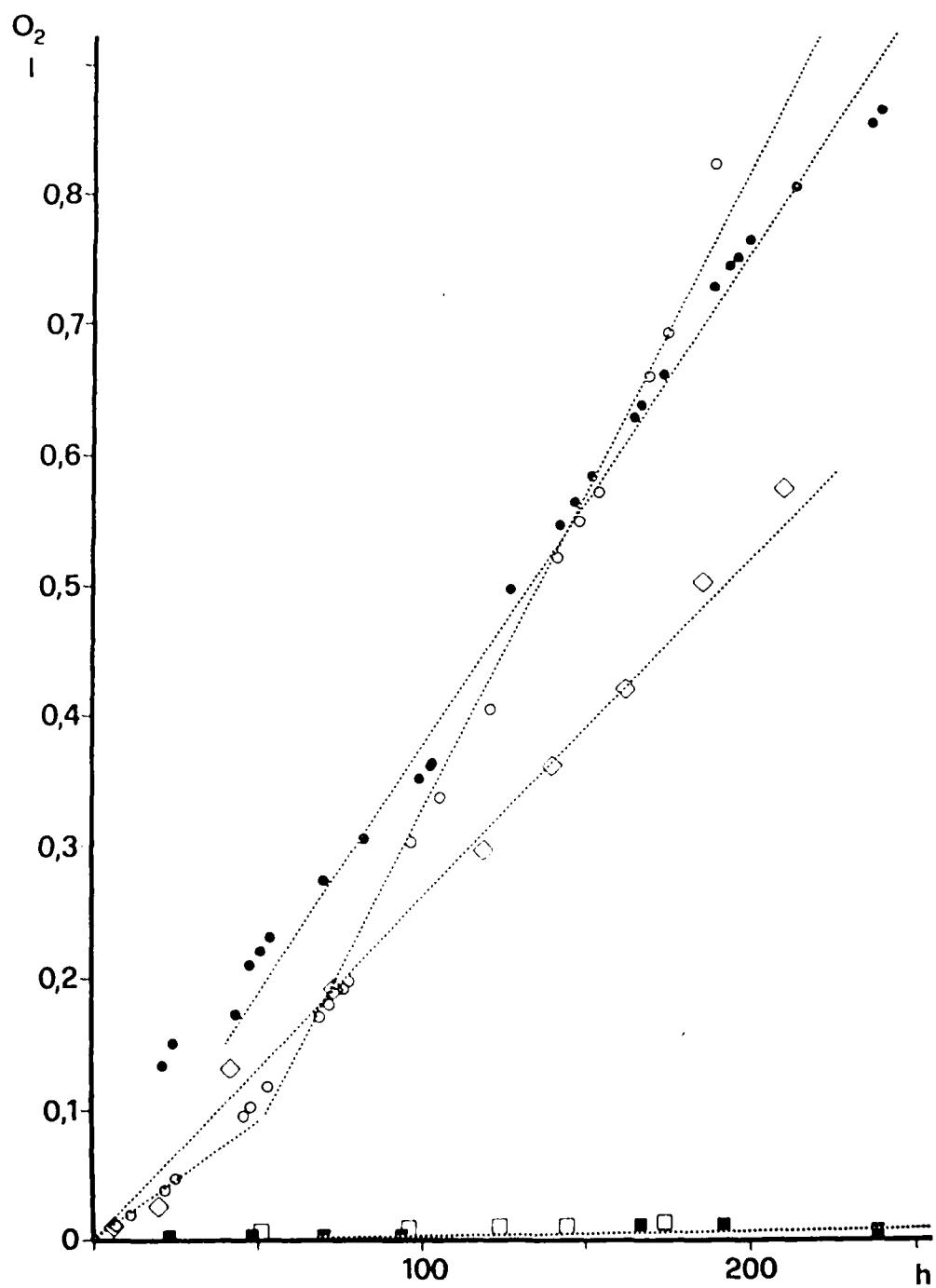
Table 2. - Rates of oxygen evolution in different microemulsions<sup>f</sup> containing  $H_2O_2$  (15°C)

A	$(4.69 \pm 0.56) \times 10^{-8} \text{ mol s}^{-1}$
B	$(6.36 \pm 0.70) \times 10^{-8} \text{ mol s}^{-1}$
C	$(3.26 \pm 0.36) \times 10^{-8} \text{ mol s}^{-1}$
D	$10^{-10} \text{ mol s}^{-1}$
E	$10^{-10} \text{ mol s}^{-1}$

<sup>f</sup> s. figure 1

In order to calculate ratios between rates of  $H_2O_2$  decomposition and  $O_2$  evolution, the above rates must be transformed for units of  $M \cdot s^{-1}$  taking into account the volume of the reaction mixture used (40 ml). Table 3 shows the corresponding results.

Figure 2. - Evolution of  $O_2$  upon decomposition of  $H_2O_2$  in different microemulsions;  $15^\circ C$



f c figura 1

**Table 3.** - Rates of oxygen evolution for 1 l of reaction mixture (15°C) and ratios between rates of hydrogen peroxide decomposition and oxygen evolution for different microemulsions<sup>f</sup>

	oxygen evolution M·s <sup>-1</sup>	ratio $\Delta H_2O_2/\Delta O_2$
A	$(1.17 \pm 0.14) \times 10^{-6}$	$3.5 \pm 0.7$
B	$(1.60 \pm 0.16) \times 10^{-6}$	$1.8 \pm 0.4$
C	$(8.15 \pm 0.90) \times 10^{-7}$	$1.9 \pm 0.4$

<sup>f</sup> s. figure 1

It becomes apparent from these calculations that under conditions of  $H_2O_2$  decomposition as chosen in microemulsion A, the mechanistic scheme indicated is almost optimally followed. Although, the ratio complies within the limits of error with the required factor of 3, the rate of oxygen evolution might be smaller as expected due to reactions generally described in equation 6.



Or oxygen production (reaction 5) may be intercepted by reactions as



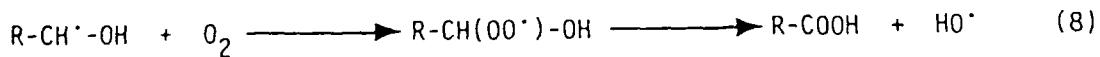
The fact that the predicted ratio is found in microemulsion A can be interpreted that under those experimental conditions  $HO^\cdot$  radicals are quantitatively trapped and that secondary reactions are of minor importance. It is, however, intriguing to see this ratio drop to 1.8 as more *n*-butanol is added (microemulsion B). The experimental results (figures 1 and 2) indicate that this change is mainly due to a slower decomposition of  $H_2O_2$ , whereas  $O_2$  evolution seems slightly enhanced. We may deduce that

- 1) dismutation of  $H_2O_2$  (reaction 2) and subsequent dismutation of  $O_2^-$  (reaction 5) proceed with comparable rates in microemulsions A and B, respectively.
- 2) decomposition of  $H_2O_2$  seems to be compensated by some process reforming hydrogen peroxide, but remaining independent of the superoxide produced intermediately.

This process would be actually growing in importance, when compared to hydrogen abstraction from the surfactant molecule (with an irreversible loss of  $H_2O_2$  (reaction 3)), as the concentration of n-butanol is increased by a factor of 6.

The corresponding butyric acid is readily produced and leads to the precipitation of the surfactant when the decomposition of  $H_2O_2$  is allowed to continue for more than 300 h. Although, the production of both butyric aldehyde and butyric acid has been qualitatively proven, quantitative analysis in function of reaction time have not yet been undertaken. From kinetic experiments, where up to 10% of butyric aldehyde have been added to A, we know, however, that the oxidation of the aldehyde yielding the corresponding butyric acid does not influence the overall rates of  $H_2O_2$  decomposition and  $O_2$  evolution.

The effect of the concentration of dissolved oxygen on the actual rate of the decomposition of hydrogen peroxide might be due to a sequence of reactions enhancing the reformation of  $H_2O_2$ , e.g.



In fact, figure 1 shows a slower decomposition of  $H_2O_2$  in D, an experiment where  $H_2O_2$  is decomposed in medium B under the pressure of the produced oxygen.

We must admit that the slight overpressure of oxygen during volumetric measurements of oxygen production might also reduce somewhat the rate of hydrogen peroxide decomposition and, thus, effect the stoichiometric ratio.

t-Butanol being the standard trapping agent of HO<sup>·</sup> radicals in radiolysis experiments<sup>3</sup>, we may assume that no secondary reactions of importance may interfere and reform hydrogen peroxide. Nevertheless, we have no means to assume experiments with microemulsion C as standard, due to the very low stoichiometric ratio. In fact, we hope to receive more data from perfluorinated and mixed, perfluorinated/perhydrogenated media, in which t-butanol could be used as the only hydrogenated component, enabling us to work out further details of the kinetics and mechanisms of H<sub>2</sub>O<sub>2</sub> decompositon.

The main problem to address is the **observed enhancement of the H<sub>2</sub>O<sub>2</sub> decomposition with laurate aggregates**. Since the rate of this decomposition depends mainly on the concentrations of the two dismutating species and, hence, on the acidity of the medium, macroscopic pH values are of great interest (table 4).

**Table 4.** - Macroscopic pH values measured in different homogeneous and microheterogeneous systems

	pH <i>t</i> <sub>0</sub>	pH <i>t</i> ~ 200 h
H <sub>2</sub> O <sub>2</sub> (30%)	3.7	3.7
A	7.6	7.0
G <sup>g</sup>	9.5	9.5
sodium laurate (H <sub>2</sub> O)	10.2 <sup>h</sup>	10.2 <sup>h</sup>
C	8.0	8.0
E	1.3	1.3
H <sup>i</sup>	6.2	6.2
SDS (H <sub>2</sub> O)	6.2	6.2
SDS / H <sub>2</sub> O <sub>2</sub> (30%)	1.3	1.2
F	3.0	3.0

<sup>g</sup> like A, but without H<sub>2</sub>O<sub>2</sub>

<sup>h</sup> crystals redissolved upon heating

<sup>i</sup> like E, but without H<sub>2</sub>O<sub>2</sub>

In accord with the mechanistic scheme of the oxidation of n-butanol, the production of the corresponding butyric acid will acidify the medium (table 4, A); nevertheless, this acidification has no observable effect on the kinetic measurements (figures 1 and 2).

In general, addition of  $H_2O_2$  to all microemulsions reduces the macroscopic pH. In strong acidic reaction mixtures (e.g. E and F) the decomposition of  $H_2O_2$  cannot take place at a detectable rate.

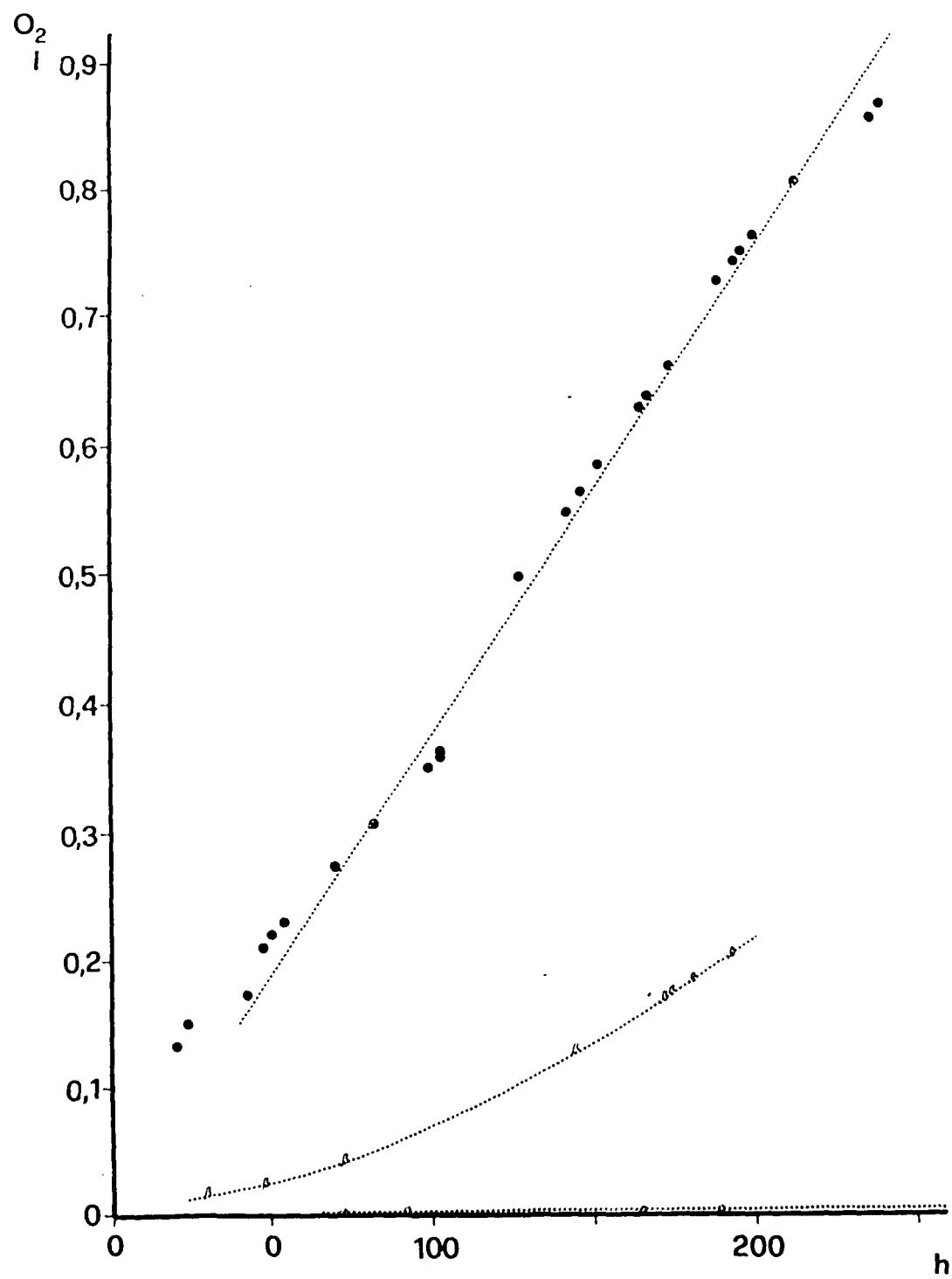
Evidence for the catalyzed decomposition of  $H_2O_2$  by laurate aggregates is given by the data shown in figure 3. In fact,  $H_2O_2$  decomposition has been measured in  $H_2O$  at pH values corresponding to those of systems A and F. The data show clearly that decomposition of  $H_2O_2$  is enhanced in A.

We interpret the enhancement of  $H_2O_2$  decomposition in A as a consequence of a stronger deprotonation of  $H_2O_2$  at the anionic interface and subsequent repulsion of  $HO_2^-$  into the bulk aqueous phase. At the same time, the carboxylate interface exhibits buffer characteristics leading to a practically constant rate of decomposition until the surfactant precipitates as a consequence of the accumulated concentration of butyric acid produced. In contrast, cationic surfaces might adsorb  $HO_2^-$ , hence reducing its concentration in the bulk aqueous phase.

Pursuing this working hypothesis, the slower decomposition of  $H_2O_2$  in B and C might then be explained by a shielding effect, due to variations of the concentration and nature of the cosurfactant, reducing the interaction of the ionic surfactant with the bulk phase and the constituents dissolved therein.

We deduce from this large series of experiments that the original choice of carboxylate surfactants for the catalysis of the decomposition of  $H_2O_2$  has shown its success, and experiments will be carried out with corresponding perfluorinated compounds, thus, creating inert media for oxidation reactions with  $HO^-$  radicals under optimal conditions.

Figure 3. - Evolution of  $O_2$  upon decomposition of  $H_2O_2$  in different media: A (●),  $H_2O_2$  (30%), pH = 7.2 ( $\beta$ ),  $H_2O_2$  (30%), pH = 3.6 ( $\alpha$ ); 15°C



### 3. Singlet oxygen quenching by N-methyl phenothiazine

Singlet oxygen luminescence (1270 nm) is currently measured in function of the concentration of added N-methyl phenothiazine. The corresponding Stern-Volmer relation does not seem to be linear indicating complex or exciplex formation between sensitizer (rose bengal) and singlet oxygen quencher. A detailed mechanistic discussion will be made after the ir measurements are completed and will be submitted in the 1st Periodic Report of the second year of contract (1986/1987).

### 4. References

- <sup>1</sup> A.M. Braun, DAJA45-85-C-0026, 2nd Periodic Report
- <sup>2</sup> B.H.J. Bielski, H.W. Richter, J.Amer.Chem.Soc. **99**, 3019 (1977)  
B.H.J. Bielski, A.O. Allen, J.Phys.Chem. **81**, 1048 (1977)
- <sup>3</sup> M.G. Simic, M.Z. Hoffmann, J.Amer.Chem.Soc. **99**, 2370 (1977)

### 5. Financial statement

As of June 30, 1986, SFR 48948.15 have been paid in salaries leaving a deficit taken up by our group of \$ 540.55.

Lausanne, September 22, 1986

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André M. Braun

## APPENDIX

### Participating scientific personnel

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